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Using positive pressure to produce a sub-micron single-crystal column of cesium iodide (CsI) for scintillator formation

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ABSTRACT

The scintillator can be directly coupled to a commercial CCD and has the fastest response time (several ns) for real-time radiography. Most scintillator material production uses an expensive vacuum deposition process or a single-crystal growth method. This work reports the development of a cost-effective way to prepare sub-micron scintillator cesium iodide (CsI) columns in a ceramic anodic aluminum oxide (AAO) template by a positive pressure penetration method. Positive pressure can decrease the iodine vapor pressure and increase the CsI sublimation point up to the CsI melting point. Because the CsI melt is confined to an AAO channel with a high aspect ratio, the melt easily solidifies into a stable single-crystal CsI column. The SEM images showed CsI in a single crystal with a column diameter of 440 nm, smooth surfaces, and no grain boundaries. This positive pressure penetration method enables fabrication of a single-crystal CsI column with controllable size.

1. Introduction

Inorganic crystal scintillators have medium to high stopping power due to their high density and atomic numbers. The cesium iodide CsI scintillator material is commonly used in X- or γ-ray detectors. An X-ray detector using the CsI material is well suited to a computed tomography system [1,2]. CsI has a simple cubic structure, and the cations of Cs^+ are located at each of the corners of a cube, while the center of the cube is a single anion of I^-. The percent ionic (%IC) character of a bond between the elements Cs and I may be approximated by the expression [3], where X_I and X_{Cs} are the electronegativities for the I and Cs

$$\%IC = (1 - \exp[-(0.25)(X_I = X_{Cs})]) \times 100 \quad (1)$$

Because $X_I = 2.5$ and $X_{Cs} = 0.7$, the CsI compound includes 55.5% ionic bonding and partial covalence bonding. Due to the amount of ionic bonding in CsI, CsI can be dissolved in polarized H_2O to form CsI aqueous solution. CsI has a high solubility in water, and the solubility increases as temperature increases. For example, the solubility of CsI in H_2O ranges from 44 to 205 wt% at 10 and 90 °C, respectively [4].

Dendrites, bobbles, and grain boundaries form easily in an ionic compound when an uncontrolled melt solidifies. For example, a cesium iodide (CsI) melt easily forms three-dimensional defects on the free surface. The defects in the dendrites or bobbles in the grains form inside the CsI as the melt solidifies. Such defects can affect the X- or γ-ray path in the CsI crystal and decrease the scintillation characteristics.

In our previous research [5–7], we have made pure metals, alloys, and CsI columns by vacuum and mechanical injection methods. The SEM images showed each CsI column has smooth surface without any grain boundary of single crystal structure. The XRD pattern showed most of CsI columns in AAO template presented to (110) and (200) planes [8]. This work reports the development of a convenient low-cost approach to fabricating a CsI single crystal column using a positive pressure penetration procedure and an anodic aluminum oxide (AAO) template.

2. Experimental procedure

The procedure includes AAO fabrication. CsI nano-particles form on the AAO inner pore wall, and a CsI column forms inside the AAO channel. The following details describe the formation of AAO, CsI nano-particles, and a CsI column. The experimental chemicals including $HClO_4$, $CH_3(CH_2)_3OCH_2CH_2OH$, C_2H_6O, CrO_3, H_3PO_4, $CuCl_2$,HCl, and CsI bought from Merck Company in reagent grade.

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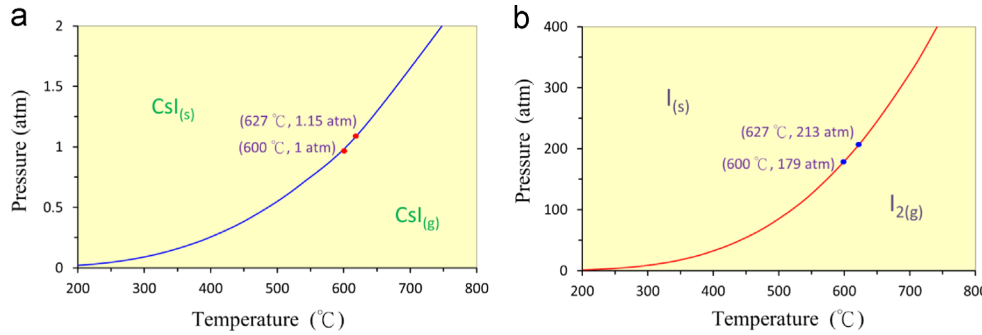

Fig. 1. The vapor pressures of CsI and I powders from 200 to 700 °C were calculated based on the Clausius Clapeyron Equation; (a) the $CsI_{(s)}$ sublimation vapor pressures are 1 atm and 1.15 atm at 600 °C and 627 °C, (b) the $I_{(s)}$ sublimation vapor pressures are 179 atm and 213 atm at 600 °C and 627 °C.

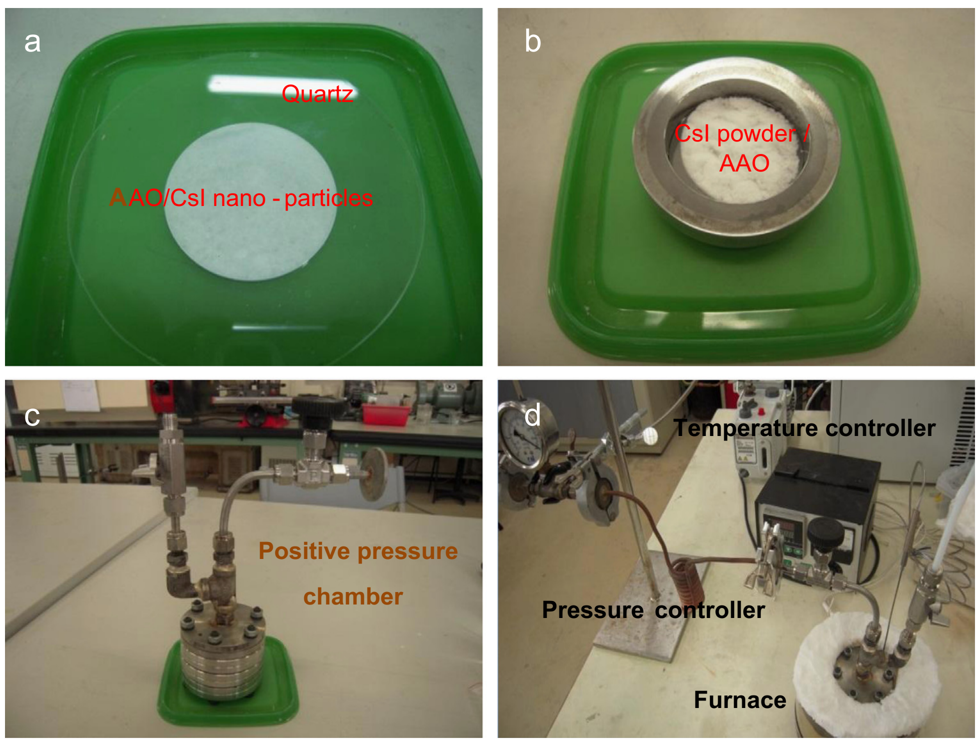

Fig. 2. The experimental setup for CsI column fabrication by CsI melt, AAO, and a high temperature positive pressure chamber; (a) AAO/CsI nano-particle template, (b) CsI powder on the AAO template, (c) AAO template/CsI powder in a positive chamber, and (d) heating CsI powder to the melting point.

AAO template: AAO film was made by anodization procedure, the steps including: (a) electrolytic polishing of Al substrate (15 vol% $HClO_4$ + 15 vol% $CH_3(CH_2)_3OCH_2CH_2OH$ + 70 vol% C_2H_6O, at 42 V), (b) 1st anodization (1 vol% H_3PO_4, at 200 V), (c) removal of 1st anodization film (1.8 wt% CrO_3 + 6 vol% H_3PO_4 + 92 vol% H_2O at 70 °C), (d) 2nd anodization (1 vol% H_3PO_4, at 200 V), (e) pore widening (5 vol% H_3PO_4, for 4 h), and (e) removal of Al substrate (8 wt% $CuCl_2$ + 5 vol% HCl + 85 vol% H_2O, for 3 min).

CsI nano-particles: In order to facilitate the CsI melt into the AAO template, CsI nano-particles were first formed on the AAO inner pore wall by wet deposition method (1 wt% CsI, at 25 °C for 3 min) and then the CsI nano-particles were sintered in an atmosphere furnace (400 °C for 5 min).

CsI column: The AAO sample with CsI nano-particles adhered and CsI powder on the surface was put on a quartz slice first, and then the AAO sample/quartz combination was placed inside a positive pressure chamber (10 atm Ar gas) and heated (650 °C for 1 min). Under these conditions, the CsI melt could flow into the AAO template. The microstructure and composition of the fabricated samples were studied using scanning electron microscope (SEM, JEOL 7400) and X-ray energy dispersive spectroscopy (EDS, Inca X-Stream).

3. Results and discussion

The sublimation, melting, and boiling points of cesium iodide compound are 600 °C, 627 °C, and 1277 °C under 1 atm, respectively. Therefore, the CsI vapor appears before the melting point. When the chamber pressure is less than 1 atm, the CsI has a lower sublimation point. The relationship between the sublimation point and pressure can be evaluated by the Clausius Clapeyron equation [9], where P, ΔH, T, R, and C are pressure (atm), enthalpy of vaporization (J/mole K), temperature (K), gas constant (8.314/J), and integration constant, respectively

$$\left(d\ln P = \frac{\Delta H}{RT^2} dT \quad or \quad \ln P = \frac{-\Delta H}{RT} + C \right) \tag{2}$$

Because CsI has vaporization enthalpy of 33,205 (J/mole K) [10] at 600 °C under 1 atm, the integration constant of CsI can be